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(54) Title: METHOD OF DISPENSING A DETERGENT COMPOSITION

(57) Abstract

The present invention relates to a method of dispensing a softening laundry detergent comprising clay and laundry surfactant as a tablet through a dispensing device in a washing machine.

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METHOD OF DISPENSING A DETERGENT COMPOSITION

Field of the Invention

This invention relates to a method of dispensing softening laundry compositions comprising clay and surfactant into the wash water of a washing machine through a net or similar dispensing device in the washing machine.

Background of the Invention

It is known to provide detergent compositions in the form of tablets made by compacting a particulate detergent composition. Usually a small amount of binder is included in the composition in order to promote the integrity of the tablets.

Although it is necessary that the tablets should have good integrity before use, it is necessary also that they should disintegrate rapidly during use, when contacted with wash water. It is known to include a disintegrant which will promote disintegration of the tablet. Various classes of disintegrant are known, including the class in which disintegration is caused by swelling of the disintegrant. Various swelling disintegrants have been proposed in the literature, with the preference being directed predominantly towards starches, celluloses and water soluble organic polymers. Inorganic swelling disintegrants such as bentonite clay have also been mentioned, for instance in EP-A-466,484.

In that disclosure, the same material acts as binder and disintegrant. It is also mentioned therein that the disintegrant may give supplementary building, anti-redeposition or fabric softening properties. The amount of disintegrant is preferably 1 to 5%. It is proposed in EP-A-466,484 that the tablet may have a heterogeneous structure comprising a plurality of discrete regions, for example layers, inserts or coatings.

In WO98/40463 it is proposed to introduce the disintegrant substantially only in granular form.

It is known to provide softening laundry compositions in powdered form containing softening clay and laundry surfactant. Dispensing these effectively into the wash water in a washing machine can cause some difficulties because of the need to avoid gelling of the composition. JP-A-9/87696 is concerned with tablets containing a non-ionic detergent composition with a non-ionic surfactant as the main component and in particular is concerned with preventing the non-ionic surfactant from oozing out of the tablets during storage, and it is also concerned with the fact that the non-ionic surfactant causes a loss in the softening effect that would be expected when a softening clay is included. It describes the formation of tablets containing finely divided clay mineral, together with a finely divided oil absorbing carrier, and a disintegrant. It does not discuss how the tablets are dispensed into the wash water and so presumably they are added direct into the wash water.

If a laundry softening tablet is formulated, it can be difficult to achieve rapid dispersion of the tablet because of the high concentration of materials which are liable to form gels, and these can include the clay in some instances, and flocculant (when present).

It would convenient to be able to dispense softening tablets into the wash liquor in a washing machine in a manner which helps to minimise or reduce gelling and which maximises the rate of solution and dispersion of the tablets into the wash liquor.

Summary of the Invention

According to the invention there is provided a method of washing and softening fabrics in wash water in a washing machine comprising placing a softening laundry detergent composition into a dispensing device, and introducing the dispensing device into the washing machine, wherein the composition is in the form of at least one tablet which comprises clay and surfactant.

The tablet preferably comprises at least 5% clay by weight of the tablet. The laundry surfactant may constitute at least 5% by weight of the tablet. Preferably the tablet includes flocculant for the clay.

The tablet may be multi-regional, with one or more discrete first regions and one or more discrete second regions, the clay being more highly concentrated in the or each first region than in the or each second region.

Detailed Description of the Invention

The tablets disperse very satisfactorily from the dispensing device since the clay in the tablet ensures break up is rapid, even when the overall composition might be expected to give some gelling problems. In particular, the method gives better dispersion than when the tablet is introduced direct into the drum or into the dispensing drawer of the washing machine.

The dispensing devices which may be used include flexible devices, such as nets or pouches, and rigid devices, including dosing balls, all having holes through which dispersed tablet components may permeate. Flexible nets are particularly preferred, since the relatively large holes in these devices are believed to be particularly beneficial in the dispensing method of the invention.

The dispensing device may be placed in the drum of a front-loading washing machine or may be introduced through the top of a top-loading washing machine. The dispensing device may be introduced after the machine is loaded with clothes which are to be washed and so may be placed on top of, or among, fabrics in the washing machine. Alternatively it may be introduced while the machine is empty or while it is being filled.

Generally, the tablet has a concentration of clay of greater than 5 weight % of a tablet, preferably 8%, and most preferably 10% by weight of the tablet. Generally, the upper limit of clay content is 25%, more preferably 20%, and most preferably 15% by weight of the tablet.

The tablet may be of uniform composition. Alternatively, the tablet may comprise one or more first regions and one or more second regions, and the concentration of clay or other component in the or each first region is different from the concentration in the or each second region. Preferably the concentration of clay in the or each first region is higher than in the or each second region. Thus it may be at least 1.5 times, or as much as 2 to 5 times the concentration of clay in the or each second region. The first region will

preferably have a concentration of at least 10% clay by weight of the or each first region. More than 50% of the total clay content of the tablet may be in the or each first region, preferably at least 60%, and more preferably at least 70% by weight of the tablet.

Preferably at least 50% (and preferably at least 75% and most preferably at least 90%) by weight of the clay is incorporated in the form of granules having a size above 100μm, preferably 100-1180μm, most preferably 150-850μm. This promotes disintegration. The granules usually contain clay in an amount of at least 50%, usually at least 70% and most preferably at least 90% by weight.

A particular advantage is gained by dispensing tablets which combine clay with at least 5% anionic and/or non-ionic surfactants. High concentrations of clay ensure rapid and complete disintegration of the tablet, thereby dispersing the surfactant particles and increasing the surface area exposed to contact with water. This has the effect of minimising gelling and maximising the cleaning efficiency of the detergent formulation. Preferably, the surfactant concentration in the or each first region is higher than the surfactant concentration in the or each second region of the tablet, for instance being at least 1.5 times (often 2-5 times) the concentration in the second regions.

The amount of anionic surfactant is usually greater than the total amount of non-ionic surfactant.

Preferably a clay flocculant is included in the tablet in order to promote clay deposition on fabric. There is a risk in providing clay and flocculant for clay in the same tablet in that premature flocculation may occur in the vicinity of clothing in the washing machine, resulting in inferior softening, for instance due to patchy deposition of clay on the clothing. For this reason it is preferred that the flocculant is segregated away from the clay in the tablet to minimise their interaction in the early stages of dispersion. A preferred design of tablet has discrete regions in which the flocculant is concentrated, and in which the concentration of clay is kept to a minimum. These regions may be granules or agglomerates, for example, or a layer or layers of a multi-layered tablet. Preferably at least 50% (and preferably at least 75% and most preferably at least 90%) by weight of the flocculant is incorporated in the form of granules

having a size above 100m, preferably 100-1180μm, most preferably 150-850μm. This promotes disintegration. The granules preferably contain flocculant in an amount of at least 50%, usually at least 70% and most preferably at least 90%.

When the tablets further comprise laundry enzymes and/or laundry bleach it is preferred that the enzymes are in regions having a higher clay concentration. This arrangement permits the enzymes to disperse rapidly upon tablet breakdown, and thereby become catalytically active in the very early stages of the wash. It is preferred that the bleach is more highly concentrated in those regions of the tablet which have a low or zero concentration of clay, so that the bleach is not destabilised by the clay and so that any enzymes are not prematurely deactivated.

The discrete first and second regions may be domains or other zones within the tablet, for instance created by forming the tablet from a particulate mixture containing large granules, typically above 1mm, wherein some or all of the large granules have one content and the remainder of the large granules or the remainder of the particulate mixture have a different content, thereby forming the first and second regions in the compressed tablet. Preferably, however, the tablet is a multi-layer tablet and each region is a layer. If there are three layers, the tablet is typically a sandwich having similar layers on each outer surface and a different central layer.

Different layers of the tablet may be coloured; this is particularly advisable for the first layer, or other layers containing clay, which may otherwise tend to impart an unattractive greyish tint on the tablet.

Typically the first regions contain 20-80%, often around 40-60% and usually about 50%, by weight of the tablet, with the second regions containing the remainder.

The tablets of the invention are of a size which is convenient for dosing in a washing machine. The preferred size is 10 to 150g and the size can be selected in accordance with the intended wash load and the design of the washing machine which is to be used.

Tablet Manufacture

Detergent tablets of the present invention can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

The ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet compressed using a force of less than 2500N.

The particulate material used for making the tablet of this invention can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 600g/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige(R) CB and/or Lodige(R) KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation sentering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable in, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of

components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tabletting, briquetting, or extrusion, preferably tabletting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy(R), Korch(R), Manesty(R), or Bonals(R)). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m2, preferably not exceed 30000 kN/m2, more preferably not exceed 5000 kN/m2, even more preferably not exceed 3000kN/m2 and most preferably not exceed 1000kN/m2. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc, and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Multi-layer tablets can be made by known techniques.

Coating

Solidity of the tablet according to the invention may be further improved by making a coated tablet, the coating covering a non-coated tablet according to the invention, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dispersion.

In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in

no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dispersed under alkaline conditions, or is readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1148-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

Suitable coating materials are dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. The coating material has a melting point preferably of from 40°C to 200°C.

The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point, and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. Clearly substantially insoluble materials having a melting point below 40°C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200°C are not practicable to use. Preferably, the materials melt in the range from 60°C to 160°C, more preferably from 70°C to 120°C.

By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10%, preferably from 1.5% to 5%, of the tablet weight.

The tablet coatings are preferably very hard and provide extra strength to the tablet.

In a preferred embodiment of the present invention the fracture of the coating in the wash is improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dispersion of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch: natural, modified or pregelatinized starch, sodium starch gluconate; gum: agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum; croscarmylose Sodium, crospovidone, cellulose, carboxymethyl cellulose, algenic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysacharides, ion exchange resins and mixtures thereof.

Tensile Strength

Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape.

For a cylindrical tablet, the tensile strength corresponds to the diametrical fracture stress (DFS) which is a way to express the strength of a tablet, and is determined by the following equation :

$$= \frac{2F}{\pi Dt}$$

Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet, and t the thickness of the tablet.

(Method Pharmaceutical Dosage Forms : Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section.

Effervescent

In another preferred embodiment of the present invention the tablets further comprises an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas,

i.e. $C_6H_8O_7 + 3NaHCO_3 \quad Na_3C_6H_5O_7 + 3CO_2 + 3H_2O$

Further examples of acid and carbonate sources and other effervescent systems may be found in : (Pharmaceutical Dosage Forms : Tablets Volume 1 Page 287 to 291).

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20 % and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dispersion aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dispersion aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H.A. Lieberman et all, ISBN 0-8247-8044-2.

Binders

Non gelling binders can be integrated to the particles forming the tablet in order to further facilitate dispersion.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bishexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials, and not as liquids.

<u>Clays</u>

The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays, i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays; in the first, aluminum oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectites are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)\,(OH)_2$ for the aluminum and magnesium oxide type clay, respectively. It is to be recognised that the range of the water of hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, expandable alumino-silicates useful herein are further characterised by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted herein above, the clays employed in the compositions of the instant invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ion, magnesium ion, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

smectite clay (Na) + NH_4OH _ smectite clay (NH_4) + NaOH.

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq./100 g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., around 26 meq/100 g. for an average illite clay.

Illite and kaolinite clays, with their relatively low ion exchange capacities, are preferably not used as the clay in the instant compositions. Indeed, such illite and kaolinite clays constitute a major component of clay soils and, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontonite, having an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful in the instant

compositions in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterised as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

While not intending to be limited by theory, it appears that advantageous softening (and potentially dye scavenging, etc.) benefits of the instant compositions are obtainable and are ascribable to the physical characteristics and ion exchange properties of the clays used therein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illites, which are both classes of clays having an ion exchange capacities below 50 meq/100 g., do not provide the beneficial aspects of the clays employed in the instant compositions.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays herein are available under various tradenames, for example, Thixogel #1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R.T. Vanderbilt. It is to be recognised that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the smectite-type clays having a cation exchange capacity of at least about 50 meq/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of product performance.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14Å x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

The clay is preferably mainly in the form of granules, with at least 50% (and preferably at least 75% or at least 90%) being in the form of granules having a size of at least 100µm up to 1800µm, preferably up to 1180µm, preferably 150-850µm. Preferably the amount of clay in the granules is at least 50%, usually at least 70% or 90%, of the weight of the granules.

Detersive surfactants

Non-limiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, anionics such as sulphonates, sulphates and ether sulphates. These include the conventional C11-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C20 alkyl sulfates ("AS"), the C10-C18 secondary (2,3) alkyl sulfates of the formula $CH_3(CH2)_x(CHOSO_3\text{-}M^+)$ CH_3 and CH_3 $(CH_2)_y(CHOSO_3\text{-}M+)$ CH_2CH_3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C10-C18 alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), C10-C18 alkyl alkoxy carboxylates (especially the $EO_{1\text{-}5}$ ethoxycarboxylates), the C10-18 glycerol ethers, the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, and C12-C18 alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 92/06154. Other sugar-derived

surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C12-C18 glucamides can be used for low sudsing. C10-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C16 soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful anionic, amphoteric, nonionic or cationic surfactants are listed in standard texts.

In preferred embodiments, the tablet comprises at least 5% by weight of surfactant, more preferably at least 15% by weight, even more preferably at least 25% by weight, and most preferably between 35% and 55% by weight of surfactant. The amount of anionic is preferably at least 1.5 times, generally at least 2 or 3 times, the total amount of other surfactants.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates,

such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSixO_2x+1.yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$Mz(zAlO_2)y].xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent

3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and

substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C12-C18 monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium

tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Bleach

The detergent compositions herein may contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen

bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

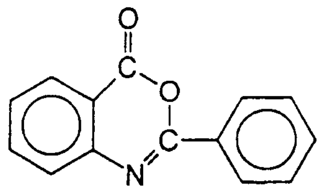
Highly preferred amido-derived bleach activators are those of the formulae:

R1N(R5)C(O)R2C(O)L or R1C(O)N(R5)R2C(O)L

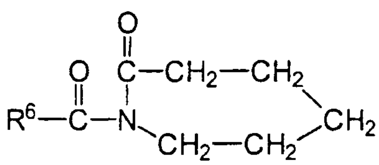
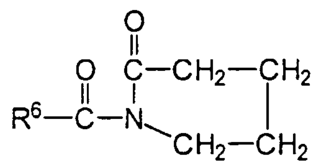
wherein R1 is an alkyl group containing from about 6 to about 12 carbon atoms, R2 is an alkylene containing from 1 to about 6 carbon atoms, R5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:


,


wherein R6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of

particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in US-A-5,246,621, US-A-5,244,594; US-A-5,194,416; US-A-5,114,606; and EP-A-549,271, EP-A-549,272, EP-A-544,440, and EP-A-544,490; Preferred examples of these catalysts include MnIV2(u-O)3(1,4,7-trimethyl-1,4,7-triazacyclononane)2(PF6)2, MnIII2(u-O)1(u-OAc)2(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO4)2, MnIV4(u-O)6(1,4,7-triazacyclononane)4(ClO4)4, MnIIIMnIV4(u-O)1(u-OAc)2-(1,4,7-trimethyl-1,4,7-triazacyclononane)2(ClO4)3, MnIV(1,4,7-trimethyl-1,4,7-triazacyclononane)- (OCH3)3(PF6), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

<u>Enzymes</u>

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated

include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see EP-A-130,756, published January 9, 1985) and Protease B (see European Patent Application 87303761.8, filed April 28, 1987, and EP-A-130,756, Bott et al, published January 9, 1985).

Amylases include, for example, -amylases described in GB-A-1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5.

Suitable cellulases are disclosed in US Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S.

Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Flocculants

Most clay flocculating polymers are fairly long chained polymers and co-polymers derived from such monomers as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone and ethylene imine. Gums, like guar gum, are suitable as well.

Preferred are polymers of ethylene oxide, acrylamide or acrylic acid. These polymers dramatically enhance the deposition of a fabric softening clay if their molecular weights are in the range of from 100 000 to 10 million. Preferred are such polymers having a weight average molecular weight of from 150000 to 5 million.

The most preferred polymer is poly (ethylene oxide). Molecular weight distributions can be readily determined using gel permeation chromatography, against standards of poly (ethylene oxide) of narrow molecular weight distributions.

The amount of flocculant is preferably 0.5-10% by weight of the tablet, most preferably about 2 to 6%.

The flocculant is preferably mainly in the form of granules, with at least 50% by weighty (and preferably at least 75% and most preferably at least 90%) being in the form of granules having a size of at least 100μm up to 1800μm, preferably up to 1180μm and most preferably 150-850μm Preferably the amount of flocculant in the granules is at least 50%, generally at least 70% or 90%, of

the weight of the granules.

Other components which are commonly used in detergent compositions and which may be incorporated into the detergent tablets of the present invention include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, brighteners, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

It should be noted that when a clay material is compressed prior to incorporation into a tablet or in a cleaning composition, improved disintegration or dispensing is achieved. For example, tablets comprising clay which is compressed prior to incorporation into a tablet, disintegrate more rapidly than tablets comprising the same clay material which has not been compressed prior to incorporation into a tablet. In particular the amount of pressure used for the compression of the clay is of importance to obtain clay particles which aid disintegration or dispensing. Further, when softening clays are compressed and then incorporated in cleaning compositions or tablets, not only improved disintegration or dispensing is obtained, but also good softening of the fabrics.

Preferably, the clay component is obtained by compression of a clay material. A preferred process comprises the steps of submitting the clay material to a pressure of at least 10MPa, or even at least 20MPa or even 40MPa. This can for example be done by tabletting or roller compaction of a clay material, optionally together with one or more other ingredients, to form a clay tablet or sheet, preferably followed by size reduction, such as grinding, of the compressed clay sheet or tablet, to form compressed clay particles. The particles can then be incorporated in a tablet or cleaning composition.

Tabletting methods and roller compaction methods are known in the art. For example, the compression of the clay can be done in a Lloyd 50K tablet press or with a Chilsonator roller compaction equipment, available form Fitzpatrick Company.

Example 1

A detergent base powder of composition A (see table 1) was prepared as follows. All the particulate materials of base composition A were mixed together in a mixing drum to form a homogenous particulate mixture. During this mixing the binder was sprayed on.

The base powder of composition A was mixed in a mixing drum and diluted with the described amounts of clay extrudate was formed using the following process, 500g of clay were mixed with 250g of distilled water. The resulting mix was fed to a Dome extruder with a screw set at a rpm of 80. The resulting mix was then screened using ASTM screen sets. The extrudates made were then dried in a Sherwood Scientific fluid bed dryer set at 90°C for 30min. The dried extrudates were screened and the oversize (particles larger than 1700μm) and the fines (particles smaller than 150μm) were removed from the mix.

Tablets were then made the following way. 42.8g of the mixture was introduced into a mould circular shape with a diameter of 5.4cm and compressed to give a tablet tensile strength (or diametrical fracture stress) of 15 kPa.

The tablet rate of dispersion was assessed as follows. 2 tablets were placed into the drum of a Miele W830 washing machine. The washing machine contained a ballast of 3kg comprising 1 kg of flat cotton, 1 kg of knitted cotton and 1 kg of polycotton. The wash cycle was set to short cycle with a wash temperature set at 40°C. 5 min after the start of the wash cycle, the machine was stopped and the contents of the machine was emptied. The machine was examined to locate chunks of undispersed tablets with a volume larger than $1cm^3$.

Example 2

Example 1 was repeated by first placing the tablets within a dispensing device offered by commercial product Ariel Futur.

Example 3

Example 1 was repeated by with tablets of composition B as indicated in table 1.

Example 4

Example 2 was repeated by with tablets of composition B as indicated in table 1.

Table 1: Detergent Base Powder Composition

	Ex A	Ex B
	%	%
Clay Extrudate	14.33	-
Flocculant Agglomerate	3.8	3.8
Anionic agglomerates 1	38	38
Cationic agglomerates	5.0	5.0
Sodium percarbonate	8	8
Bleach activator agglomerates	2.31	2.31
Sodium carbonate	17.00	31.33
EDDS/Sulphate particle	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34
Fluorescer	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027
Soap powder	1.40	1.40
Suds suppressor	2.6	2.6
Citric acid	4.0	4.0
Protease	0.45	0.45
Cellulase	0.20	0.20
Amylase	0.20	0.20
Binder		
Cationic Polymer	0.75	0.75
PEG 4000	1.25	1.25

Clay extrudate comprise 97% of montmorillonite clay and 3% water.

Flocculant raw material is polyethylene oxide with an average molecular weight

of 300,000.

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate.

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate.

Layered silicate comprises of 95% SKS 6 and 5% silicate.

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active,

Suds suppressor comprises of 11.5% silicone oil; 59% of zeolite and 29.5% of water.

It was seen that Examples 1 and 3 both gave poor dispersion. Example 4 gave some improvement but Example 2 gave a very marked improvement.

Other examples include tablets made from a powder of the following composition:

Examples A and B

Table A: Detergent base powder composition

	Ex A	Ex B
	(%)	(%)
Clay Extrudate	14.00	14.00
Flocculant Agglomerate	3.8	3.8
Anionic agglomerates 1	32	38
Anionic particle 2	2.27	2.27
Cationic agglomerates	4.0	
Sodium percarbonate	8.0	10.0
Bleach activator agglomerates	2.31	2.8
Sodium carbonate	21.066	16.57
EDDS/Sulphate particle	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34
Fluorescer	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027
Soap powder	1.40	1.40
Suds suppressor	2.6	2.6
Citric acid	4.0	4.0
Protease	0.45	0.45
Cellulase	0.20	0.20
Amylase	0.20	0.20
Perfume	1.00	1.00
Binder		
Pluriol 1000	2.0	2.0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Example C (micronised citric acid)

In composition of example B, the citric acid used was replaced with micronised citric acid. The citric acid used was ground with a coffee grinder to the following psd prior to use.

	Max level of particles bigger than 1.4 mm	Max level of particles smaller than 150um
Example B	8%	12%

	Min level of particles smaller than 150um
Example C	80%

Example D-F (phosphated composition)

	Ex D	Ex E	Ex F
	(%)	(%)	(%)
Clay Extrudate	13.00	13.00	13.00
Flocculant Agglomerate	3.5	3.5	3.5
Anionic particle	38.2	38.2	38.2
Sodium percarbonate	8.0		
Sodium perborate monohydrate		8.0	
Sodium perborate tetrahydrate			8.0
Bleach activator agglomerates	2.3	2.3	2.3
HPA sodium tripolyphosphate	15.4	15.4	15.4

Sodium carbonate	10.043	10.043	10.043
EDDS/Sulphate particle	0.19	0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.34	0.34	0.34
Fluorescer	0.15	0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate	0.027	0.027	0.027
Soap powder	1.40	1.40	1.40
Suds suppressor	2.6	2.6	2.6
Citric acid	1.0	1.0	1.0
Protease	0.45	0.45	0.45
Cellulase	0.20	0.20	0.20
Amylase	0.20	0.20	0.20
Perfume	1.00	1.00	1.00
Binder			
Pluriol 1000	2.0	2.0	2.0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.
Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

The anionic particle was a blown powder with the following composition:

	(%)
Sodium linear alkylbenzene sulphonate	17.7
Nonionic C35 7EO	2.0
Nonionic C35 3EO	5.9
Soap	0.5
Sodium tripolyphosphate, (Rhodia-Phos HPA 3.5 from Rhone Poulenc)	47.8
Sodium silicate	10.8
Sodium carboxymethly cellulose	0.4
Acrylate / maleate copolymer	2.1
Salts, moisture	12.9

Examples G and H

		Ex G	Ex H
		(%)	(%)
Clay Extrudate		14.00	14.00
Flocculant Agglomerate		3.8	3.8
Anionic agglomerates 1		32	32

Anionic particle 2		2.27	2.27
Cationic agglomerates		4.0	4.0
Sodium percarbonate		8.0	8.0
Bleach activator agglomerates		2.31	2.31
Sodium carbonate		18.066	18.066
EDDS/Sulphate particle		0.19	0.19
Tetrasodium salt of Hydroxyethane Diphosphonic acid		0.34	0.34
Fluorescer		0.15	0.15
Zinc Phthalocyanine sulphonate encapsulate		0.027	0.027
Soap powder		1.40	1.40
Suds suppressor		2.6	2.6
Arbocel TF-30-HG		5.0	
Vivapur G22			5.0
Citric acid		2.0	2.0
Protease		0.45	0.45
Cellulase		0.20	0.20
Amylase		0.20	0.20
Perfume		1.00	1.00
Binder			
Pluriol 1000		2.0	2.0

Clay extrudate comprise 97% of CSM Quest 5A clay and 3% water

Flocculant raw material is polyethylene oxide with an average molecular weight of 300,000

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 81% TAED (Tetra acetyl ethylene diamine), 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Zinc phthalocyanine sulphonate encapsulates are 10% active.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning); 59% of zeolite and 29.5% of water.

Arbocel TF-30-HG and Vivapur G22 are cellulose containing disintegration agent from the Rettenmaier company

Example I-N

Example A-G are repeated by dipping the tablets made with the indicated composition in a bath comprising 80 parts of adipic acid mixed with 18.5 parts of CSM Quest 9 clay and 1.5 parts of Coasol (Coasol being a diisobutyladipate).

The tablet may also comprise a high molecular weight poly(ethyleneoxide), cellulosic disintegrant, and/ or acetate. It could also further comprise high soluble salts.

Claims

1. A method of washing and softening fabrics in wash water in a washing machine comprising placing a softening laundry detergent composition in a dispensing device, and introducing the dispensing device into the washing machine, wherein the tablet composition is in the form of at least one tablet and comprises clay and laundry surfactant.

2. A method according to claim 1 wherein the tablet comprises at least 5% by weight of clay and at least 5% by weight of laundry surfactant.

3. A method according to claim 2 wherein the tablet comprises at least 8%, preferably at least 10% by weight of clay.

4. A method according to any of claims 1 to 3 wherein the tablet comprises one or more discrete first regions and one or more discrete second regions, and the clay is more highly concentrated in the or each first region than in the or each second region.

5. A method according to claim 4 wherein the concentration of clay in the or each first region is 2 to 5 times the concentration of clay in the or each second region, and the clay concentration in the or each first region is at least 10% by weight of the or each first region.

6. A method according to claim 4 or claim 5 wherein the tablet further comprises laundry enzyme and laundry bleach, and wherein the concentration of enzyme in the or each first region is higher than the concentration in the or each second region, and the concentration of bleach in the or each second region is higher than the concentration in the or each first region.

7. A method according to any of claims 4 to 6 wherein the tablet is a multi-layer tablet, and each region of the tablet is a layer of the tablet.

8. A method according to any preceding claim wherein the tablet further comprises a flocculant for clay.

9. A method according to claim 8 in which the tablet is a compressed mass of particles and at least 50% by weight of the flocculant is present as granules which have a size of at least 100μm and which contain at least 50% by weight of the flocculant.

10. A method according to any preceding claim wherein the tablet is a compressed mass of particles, and at least 50% by weight of the clay is present as granules, which have a size of at least 100μm, and which contain at least 50% by weight clay.

11. A method according to any preceding claim wherein the clay is a bentonite clay.

12. A method according to any preceding claim in which the amount if anionic surfactant in the tablet is greater than the amount of non-ionic surfactant.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/10273

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/12 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 598 586 A (UNILEVER PLC) 25 May 1994 (1994-05-25)	1-3,7,11
Y	page 8, line 36 -page 9, line 16	1-4,6,7
A	page 17, line 35 - line 37	5,12

Y	EP 0 466 484 A (UNILEVER PLC) 15 January 1992 (1992-01-15) cited in the application	1-4,6,7
A	page 2, line 50 - line 57 page 3, line 57 -page 4, line 3 page 5, line 25 - line 34 page 6, line 20 - line 22 claim 1	5,8-12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 August 2000	22/08/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/10273

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 320 255 A (PROCTER & GAMBLE) 17 June 1998 (1998-06-17) claims 1,13,14 page 50, paragraph 1 - paragraph 2 page 53, paragraph 1 -page 55, paragraph 1 ---	1-3,8
X	GB 2 303 142 A (PROCTER & GAMBLE) 12 February 1997 (1997-02-12) claims 1,12 page 37, paragraph 2 page 39 -page 40 page 32, paragraph 2 - paragraph 3 ---	1-3,8,11
A	EP 0 866 118 A (PROCTER & GAMBLE) 23 September 1998 (1998-09-23) page 15, line 15 -page 17, line 4 ---	1,6,8,12
A	PATENT ABSTRACTS OF JAPAN vol. 199, no. 707, 31 July 1997 (1997-07-31) & JP 09 087696 A (LION CORP), 31 March 1997 (1997-03-31) cited in the application abstract ---	1
A	DE 44 04 279 A (HENKEL KGAA) 17 August 1995 (1995-08-17) column 4, line 67 -column 12, line 25 claims 1,9-13; example 5 ---	1,6,7, 11,12
A	EP 0 255 779 A (UNILEVER PLC) 10 February 1988 (1988-02-10) claims 1-3,5 ---	1
P,X	WO 99 40171 A (UNILEVER PLC) 12 August 1999 (1999-08-12) page 3, line 12 -page 6, line 2 page 12, line 11 -page 15, line 20 page 21, line 5 -page 22, line 24 claims -----	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/10273

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0598586	A	25-05-1994	DE	69307660	D	06-03-1997
			DE	69307660	T	07-05-1997
			ES	2097994	T	16-04-1997
EP 0466484	A	15-01-1992	AU	635141	B	11-03-1993
			AU	8030691	A	16-01-1992
			BR	9102951	A	11-02-1992
			CA	2046453	A,C	14-01-1992
			DE	69109192	D	01-06-1995
			DE	69109192	T	31-08-1995
			ES	2071924	T	01-07-1995
			JP	2046192	C	25-04-1996
			JP	4253800	A	09-09-1992
			JP	7068557	B	26-07-1995
			KR	9504826	B	13-05-1995
			US	5360567	A	01-11-1994
			ZA	9105455	A	31-03-1993
GB 2320255	A	17-06-1998	EP	0944710	A	29-09-1999
			WO	9826038	A	18-06-1998
GB 2303142	A	12-02-1997	CA	2226621	A	30-01-1997
			EP	0845024	A	03-06-1998
			WO	9703164	A	30-01-1997
EP 0866118	A	23-09-1998	GB	2323384	A	23-09-1998
			CA	2232205	A	20-09-1998
JP 09087696	A	31-03-1997	NONE			
DE 4404279	A	17-08-1995	WO	9521908	A	17-08-1995
			EP	0743978	A	27-11-1996
			EP	0965565	A	22-12-1999
			US	5900399	A	04-05-1999
EP 0255779	A	10-02-1988	AU	590435	B	02-11-1989
			AU	7609187	A	04-02-1988
			BR	8703862	A	29-03-1988
			JP	1604125	C	22-04-1991
			JP	2027471	B	18-06-1990
			JP	63042977	A	24-02-1988
			KR	9009221	B	24-12-1990
			ZA	8705589	A	29-03-1989
WO 9940171	A	12-08-1999	AU	2720699	A	23-08-1999